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PHOTOREDUCTION OF 2-PIPERIDINOANTHRAQUINONE BY AN ELECTRON TRANSFER VIA THE UPPER EXCITED $n\pi^*$ TRIPLET STATE

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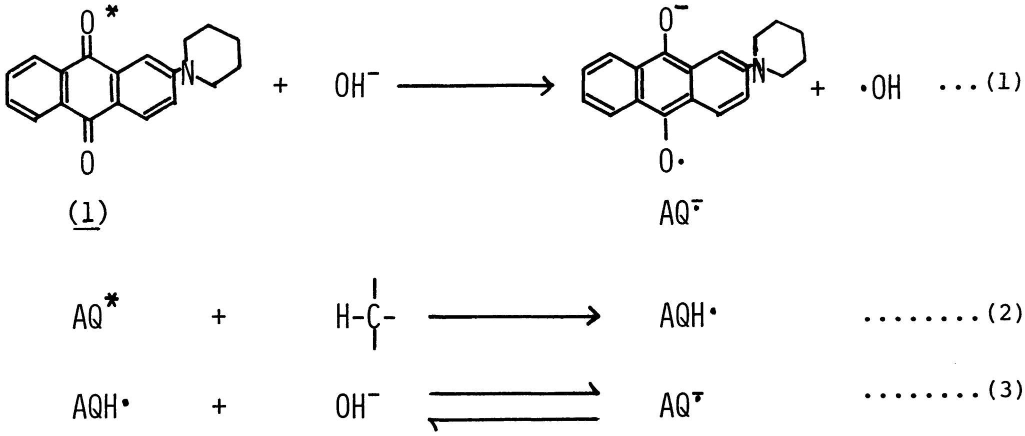
The photoreduction of 2-piperidinoanthraquinone (1) by an electron transfer from hydroxide ion in 4:1 2-propanol-water mixture was reinvestigated. The reaction proceeded on irradiation with the light of λ = 365 nm, but hardly did with that of λ>420 nm which excites (1) exclusively to the ^{1}CT level. The fluorescence of (1) was not affected by hydroxide ion. 1,3-Cyclohexadiene as a triplet quencher retarded the photoreduction. The reactive state of (1) in the photoreduction was concluded to be not the intramolecular excited CT state, but the upper excited $n\pi^*$ triplet state.

In the photochemistry of anthraquinone derivatives, it has long been emphasized that the excited triplet $n\pi^*$ state is very reactive, while the intramolecular CT one has little reactivity.[1) However, recently we have found a new photosubstitution reaction of aminohaloanthraquinones by amines under the irradiation of the visible light and demonstrated that the intramolecular CT state is reactive in the reaction.[2) A.K.Davies et al also postulated that the intramolecular CT one is reactive in the photoreduction of 2-piperidinoanthraquinone (1) by an electron transfer from hydroxide ion or alkoxide ion on irradiation with the light of λ = 365 nm.[3) However, an ambiguity remaines in their conclusion on the reactive state ; there is another possibility that the photoreduction proceeds via the upper excited $T_2(^3n\pi^*)$ level from the viewpoint of the energy diagram of (1) depicted in Fig.. Hence, we reinvestigated this photoreduction of (1) by hydroxide ion and, contrary to Davies's conclusion, we found that the reaction proceeds not via the intramolecular CT state but via the upper excited $T_2(^3n\pi^*)$ state.

(1) (1.00×10^{-4} mol/dm^3) and hydroxide ion in 4:1 2-propanol-water mixture was irradiated with the monochromatic light of λ = 365 nm under nitrogen atmosphere. The absorption bands at λ= 402, 476, and λ>650 nm, assigned to the radical anion of (1), increased with irradiation. The isosbestic points were obsereved at λ = 377, 498, and 570 nm. An introduction of air to the irradiated reaction mixture caused rapid dissapearance of the radical anion of (1), and (1) was recovered unchanged. A similar effective photoreduction was also obsereved in aqueous acetonitrile which is considered to have little reactivity toward a conventional hydrogen atom abstraction. The reciprocal of the relative quantum yield of the production of the radical anion of (1) ($1/\Phi$) was found to be linear with the reciprocal of the total amount of hydroxide ion added to the reaction system ($1/[OH^-]$). These results suggest that the radical anion of (1) is produced not by a conventional hydrogen abstraction by the excited (1) from the solvent followed by a deprotonation (eq. 2,3), but by an electron transfer from hydroxide ion (eq. 1).



The radical anion of (1) was stable as an end product in the reaction system. Hence, it was supposed that most of the hydroxide radical, a powerful oxidizing agent, produced in the reaction system along with the radical anion of (1)(eq. 1) would abstract a hydrogen atom from 2-propanol to produce water molecule and the formation of hydrogen peroxide might be suppresed.

If the photoreduction of (1) by hydroxide ion proceeds via ^{1}CT level, (1) should be photoreduced on irradiation with the light of λ>420 nm which excites (1) exclusively to the ^{1}CT level. And the fluorescence of (1) should be quenched by hydroxide ion to such an extent as is predicted from the linear plot between $1/\Phi$ and $1/[OH^-]$.

However, as shown in Table, the radical anion of (1) was hardly produced on irradiation with the light of $\lambda > 420$ nm, and the fluorescence intensity of (1) was not affected by the presence of hydroxide ion ($1 \times 10^{-3} \sim 1 \times 10^{-1}$ mol/dm^3). These contradicting results clearly indicate that the photoreduction of (1) does not proceed via the ^{1}CT level, but via the upper excited level which can be populated on irradiation with the light of λ = 365 nm. Moreover, the photoreduction was retarded by the addition of 1,3-cyclohexadiene as a triplet quencher and a linear Stern-Volmer plot was obtained with the value of $k_q \cdot \tau$ = 20 dm^3/mol ($[OH^-]$ = 0.1 mol/dm^3).

Since the triplet level of 1,3-cyclohexadiene (E_T = 52 kcal/mol) is higher than the T_1(^{3}CT) of (1) and lower than the T_2($^3n\pi^*$), it was concluded that the photoreduction of (1) by an electron transfer from hydroxide ion proceeds via the T_2($^3n\pi^*$) level on irradiation with the light of λ = 365 nm. These conclusion are schematized in Fig..

Table Effect of the wavelength of irradiation on the production of $AQ^{\overline{\cdot}}$

Wavelength of irradiation	Relative quantum yield
313 nm	1.0
365 nm	1.0
>420 nm	0.003

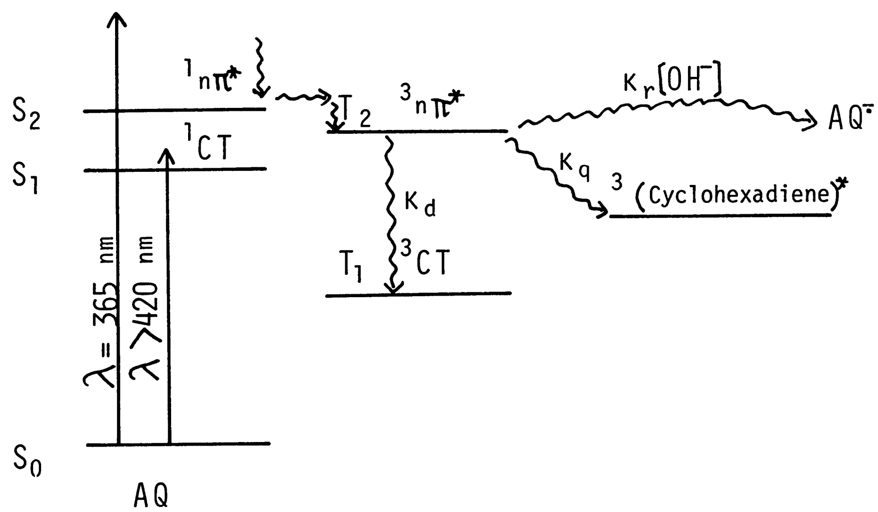


Fig. Energy diagram of (1) and the reaction scheme

Supposing that the quenching rate constant k_q by 1,3-cyclohexadiene is a diffusion controlled one (10^{10} $dm^3/mol\cdot s$), the value of $k_q\cdot\tau$ and k_d/k_r (5.0×10^{-2} mol/dm^3) given by the ratio between the slope and the intercept in the plot of $1/\Phi$ against $1/[OH^-]$ indicate that $k_r = 3.3 \times 10^9$ $dm^3/mol\cdot s$ and $k_d = 1.7 \times 10^8$ s^{-1}. The value of k_d revealed that the $T_2(^3n\pi^*)$ level of (1) in 4:1 2-propanol-water mixture have a relatively long lifetime of 5.9 ns ($=1/k_d$) in spite of an upper excited level, which is considered to be characteristic of anthraquinone derivatives.[4)]

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